Message

**From:** Washington, John [/O=EXCHANGELABS/OU=EXCHANGE ADMINISTRATIVE GROUP (FYDIBOHF23SPDLT)/CN=RECIPIENTS/CN=FDC3E8CE9F1D45C4894881FF420CA104-WASHINGTON, JOHN]
**Sent:** 3/27/2018 2:18:37 PM
**To:** Libelo, Laurence [/o=ExchangeLabs/ou=Exchange Administrative Group (FYDIBOHF23SPDLT)/cn=Recipients/cn=da33642e6438407daf4c35afe870046b-Libelo, Laurence]
**Subject:** FW: M/N homologue detects of 1/0, 0/1, 1/1, 1/2, 2/1, I found nothing on 0/0 so far
**Attachments:** image2018-03-27-093459.pdf

Hey Laurence –

Can I talk you into reviewing that PFOS in Brazil manuscript I sent you earlier today?

Also take a look at the combinations of the Solvay chemical I think I might be seeing. (My subject is wrong, I did not find 1/0 yet.)

John

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**From:** Washington, John
**Sent:** Tuesday, March 27, 2018 10:01 AM
**To:** McCord, James <mccord.james@epa.gov>; Lindstrom, Andrew <Lindstrom.Andrew@epa.gov>; Strynar, Mark <strynar.mark@epa.gov>
**Subject:** M/N homologue detects of 1/0, 0/1, 1/1, 1/2, 2/1, I found nothing on 0/0 so far

Hi guys,

I still will be occupied with other stuff today, but I snuck in an early run.

I think we are getting close. But I think it still is not crystal clear regarding whether the terminal moieties -COO and -CF2COO can be lost in a) processing, b) the environment, or c) the ESI during ionization. And I think it remains unclear whether this might differ with chain length (like perhaps the shorter chains retain CF2COO more so than long chain lengths. And I still am uncertain whether observed variations I summarize below are due to 1) processing, 2) degradation (less likely at this point?), or 3) a combination of 1 and 2.

So I ran several possible transitions including (using Wang's M and N moiety assignments) shown on the attached:

i) M=0 N=0 (nondetect ND);
ii) M=0 N=1 (small peak);
iii) M=0 N=1 (decarboxylated) (large peak);
iv) M=1 N=0 (ND) (but I should try decarboxylated by analogy with ii & iii);
v) M=1 N=1 (but loss of CF2COO) (largest peak);
vi) M=1 N=1 (loss of COO) (2nd largest peak & note different elution time than v);
vii) M=1 N=1 (including CF2COO but I should try lower cone energy in the ESI) (ND);
viii) M=2 N=1 (with loss of CF2COO) (moderate peak);
ix) M=1 N=2 (with loss of CF2COO) (small peak);
x) Same as viii but with CF2COO (ND)
xi) Same as ix but with CF2COO (ND)

At this point I have run my ESI cone potential only at the same value as I use for most PFCAs.

John

**From:** Washington, John
**Sent:** Monday, March 26, 2018 4:09 PM
**To:** McCord, James <mccord.james@epa.gov>; Lindstrom, Andrew <Lindstrom.Andrew@epa.gov>; Strynar, Mark <strynar.mark@epa.gov>
**Subject:** RE: The sample is

Not yet, the moving-to-another-building people are driving me crazy, the computer IT people lost the key disk for my quantification software , and I have a journal manuscript I am late reviewing. And all I wanted to do today is play with this stuff.

I plan to try all permutations of M and N over the next days and will let you know. And how about you let me know each new discovery too.

Intuitively, for the probably most-soluble compound, I would look for evidence of the smallest, where M=0 and N=0. So looking at Wang's Fig 1, I think M=o and N=0 would be the 201 fragment (C3F6Cl) +CF2+COO. Then, you already found N=1 and M=0. How about looking for N=0 and M=1?

I plan to try all this and build 1M or 1N at a time. But first I have to get my ESI satisfactorily low.

**From:** McCord, James
**Sent:** Monday, March 26, 2018 3:54 PM
**To:** Washington, John <Washington.John@epa.gov>; Lindstrom, Andrew <Lindstrom.Andrew@epa.gov>; Strynar, Mark <Strynar.Mark@epa.gov>
**Subject:** RE: The sample is

I believe that is correct yes. I see the higher masses as well and had speculated that was there ID. I have the MS/MS spectra collected but didn't follow up.

Are there other masses you are seeing of interest that I should look for?
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James McCord

**From:** Washington, John
**Sent:** Monday, March 26, 2018 3:52 PM
**To:** McCord, James <mccord.james@epa.gov>; Lindstrom, Andrew <Lindstrom.Andrew@epa.gov>; Strynar, Mark <Strynar.Mark@epa.gov>
**Subject:** RE: The sample is

So basically, with reference to the Wang functional groups listed in his Figure 1, I suspect your 461 is for N=1 and M=0. And I think my 483 and 533 are for N=1 and M=1, but I ionized too hard in the ESI and knocked off the CF2COO (for 483) and COO (for 533).

**From:** Washington, John
**Sent:** Monday, March 26, 2018 3:42 PM
**To:** McCord, James <mccord.james@epa.gov>; Lindstrom, Andrew <Lindstrom.Andrew@epa.gov>; Strynar, Mark <strynar.mark@epa.gov>
**Subject:** RE: The sample is

When I run the 483 and the 461 in the same run, they do not co-elute – see attached. Instead the 461 co-elutes with the 367. Maybe the 461 is the 367 fragment +CF2+COO? And the 483 is the 367 fragment +CF(CF3)+O?

Based on this, I think I will try to run a lower ESI energy and look for the 533+COO – maybe it is decarboxylated easily in the ESI. And maybe when the terminus is -CF2-COO, this might be lost in vigorous ESI as well, hence 533 (without COO) and 483 (without CF2-COO). This pattern also might fit with the observation on my attached runs that 461 has a peak area of only 500 but the 367 has a peak area of >15000, i.e., losing CF2COO in ESI.

I know when I have run High-energy ESI on purpose for PFCAs, the COO is lost in the ESI.

**From:** McCord, James
**Sent:** Monday, March 26, 2018 12:40 PM
**To:** Washington, John <Washington.John@epa.gov>; Lindstrom, Andrew <Lindstrom.Andrew@epa.gov>; Strynar, Mark <Strynar.Mark@epa.gov>
**Subject:** RE: The sample is

I believe the 482 is the sodium adduct of the 460. Depending on the buffer conditions and electrospray we get different adducts.

There are definitely longer and shorter versions of the compounds in the water as well, they are just much lower in abundance (possibly solubility related?) and I haven't tabulated them yet.
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James McCord

**From:** Washington, John
**Sent:** Monday, March 26, 2018 11:38 AM
**To:** McCord, James <mccord.james@epa.gov>; Lindstrom, Andrew <Lindstrom.Andrew@epa.gov>; Strynar, Mark <Strynar.Mark@epa.gov>
**Subject:** RE: The sample is

Hey guys,

Adding to confusion, I wonder if we might be seeing different ethers??

James' water had 460.926 for example (and fragmenting to 366.9XXX?). And most recently for soil, I had three separate elution times for precursors at 532.927, 482.929, and 366.941.

When I formula searched the 460.926 water mass (assuming a single Cl, is this correct?), a small formula error came back as C8ClF14O4. For the three soils masses, possible formulae were C9ClF18O3 (as shown in the Z. Wang figure), C8ClF16O3 (as though the terminal CF2 on Wang figure was not present), and C6ClF12O2.

So James' 460.926 water mass looks similar to my soil 482.929 soil mass except +O-2F maybe? And three elution times/precursor masses for the soils suggests three separate compounds as well?

John

**From:** McCord, James
**Sent:** Monday, March 26, 2018 7:49 AM
**To:** Lindstrom, Andrew <Lindstrom.Andrew@epa.gov>; Strynar, Mark <Strynar.Mark@epa.gov>; Washington, John <Washington.John@epa.gov>
**Subject:** RE: The sample is

So it is possible that we are seeing waterway emission that Is tidally backflushed to the upstream tributary?
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James McCord

**From:** Lindstrom, Andrew
**Sent:** Monday, March 26, 2018 6:31 AM
**To:** McCord, James <mccord.james@epa.gov>; Strynar, Mark <Strynar.Mark@epa.gov>; Washington, John <Washington.John@epa.gov>
**Subject:** FW: The sample is

All,

I think this is the sample that looks like it has high levels of the Solvay chloro-fluoro ether.

Andy

**From:** Bergman, Erica [mailto:Erica.Bergman@dep.nj.gov]
**Sent:** Friday, March 23, 2018 3:51 PM
**To:** Lindstrom, Andrew <Lindstrom.Andrew@epa.gov>
**Subject:** RE: The sample is

Andy,

The surface water sample number PFTSWDUP1 was collected with surface water sample PFTSW015, which was collected in Woodbury Creek, near the confluence of the Delaware River. This location is upriver from the Solvay site, but still tidally influenced. Note that one of the residential private wells located along Woodbury Creek (Clement Drive) had the highest levels of PFNA (1,500 ng/L) found in a private well near the Solvay site.

On map below: Little red dot is the sample location; Solvay site is circled in red; larger red marker is Clement Drive.


**From:** Lindstrom, Andrew <Lindstrom.Andrew@epa.gov>
**Sent:** Friday, March 23, 2018 9:54 AM
**To:** Bergman, Erica <Erica.Bergman@dep.nj.gov>
**Subject:** The sample is

Erica,

The sample is PFTSWDUP1 and is highlighted on the attached CoC sheet.

Thank you,

Andy